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APPROXIMATE EMISSIVITY CALCULATIONS
FOR POLYATOMIC MOLECULES. I. CO₂

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APPROXIMATE EMISSIVITY CALCULATIONS FOR POLYATOMIC MOLECULES. I. CO₂. *

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Approximate emissivity calculations for CO₂ have been carried out, as a function of optical density, at 300 and at 600°K. The calculations involve the assumption that the rotational lines overlap extensively. This condition appears to be satisfied at total pressures above about 1 atmos. Comparison of the values calculated from spectroscopic data with the emissivities tabulated by Hottel and his collaborators shows satisfactory agreement. The analysis presented in this manuscript emphasises the fact that it is possible to obtain reasonable estimates for the engineering emissivity without performing extensive analytical work, provided the physical principles are understood and the needed spectroscopic data are available.

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INTRODUCTION I.

In a series of recently published papers we have attempted to estimate the engineering emissivities of distornic molecules by utilizing basic spectroscopic constants. Tractable methods of calculation have been developed for (a) complete overlapping between rotational lines and for (b) separated rotational lines. 2 Although accurate theoretical calculations of gas emissivities from spectroscopic data for polyatomic molecules involve formidable computational difficulties, it is to be expected that approximate calculations can be carried out with relatively little effort by utilizing approximations similar to those introduced for the study of diatomic molecules. 1, 2 For CO2 it has been found that the total absorptivity at room temperature is substantially independent of pressure at pressures exceeding about 1 atmos., 3 thus indicating extensive overlapping between rotational lines. Accordingly, it is not unreasonable to base the present preliminary calculations on the assumption that extensive overlapping between rotational lines does occur. The results would be expected to apply, for example, at room temperature for total pressures in excess of 1 atmos. and at 3000°K at pressures in excess of 11 atmos. 3 Since it appears quite likely that the

⁽a) S. S. Penner, J. Appl. Phys. 21, 685 (1950);
(b) J. Appl. Mech. 18, 53 (1951); (c) S. S. Penner and D. Weber, J. Appl. Phys. 22, 1164 (1951).

^{2 (}a) S. S. Penner, M. H. Ostrander, and H. S. Tsien, J. Appl. Phys. 23, 256 (1952); (b) S. S. Penner, J. Appl. Phys. 23, 825 (1952).

³ R. J. Holm, D. Weber, and S. S. Penner, J. Appl. Phys. <u>23</u>, 1283 (1952).

actual range of validity of the results covers a larger range of total pressures, we shall not hesitate to show that calculated emissivities agree reasonably well with empirical data obtained at 1 atmos. at a temperatured of 600°K as well as at 300°K. Perhaps the most important conclusion which can be derived from the present analysis is the statement that the analytical labor involved in making approximate emissivity calculations for a polyatomic molecule with overlapping rotational lines is trivial provided the important physical principles are understood and the needed spectroscopic data are available. It is only fair to note, however, that all of the needed integrated intensity measurements have not yet been performed for CO₂ in spite of the fact that several papers dealing with intensity measurements have been published recently. 5, 6, 7

II. BASIC RELATIONS

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Theoretical considerations of intensities for various transitions of the CO₂ molecule were summarised by Dennison a number of years ago. ⁸ We shall reproduce here the parts of the malysis which are useful for making approximate emissivity estimates on CO₂.

W. H. McAdams, Heat Transmission, McGraw-Hill Book Co., New York 1942, Chapter III by H. C. Hottel.

⁵ A. M. Thorndike, J. Chem. Phys. <u>15</u>, 868 (1947).

^{6:} D. F. Eggers, Jr., and B. L. Crawford, Jr., J. Chem. Phys. 19, 1554 (1951).

⁷ D. Weber, R. J. Holm, and S. S. Penner, J. Chem. Phys. <u>20</u>, 1820 (1952).

⁸ D. M. Dennison, Rev. Mod. Phys. <u>3</u>, 280 (1931).

Frequencies (3) and wave numbers (3) corresponding to transitions between fixed energy levels are given by the Bohr frequency condition

$$v = c \omega = (\Delta W'_V + \Delta W'_R)/h \tag{1}$$

where ΔW_V and ΔW_R represent, respectively, the changes in vibrational and rotational energy corresponding to the frequency v, h is Planck's constant, and c represents the velocity of light. According to the results of Dennison and Adel, v, the rotational v, and v wibrational v, energies for v, are given, respectively, by the expressions

$$W'_{R} = hc(j^{2} + j - \mathcal{L}^{2}) \left[0.3925 - 0.00058 \left(n_{1} + \frac{1}{2} \right) + 0.00045 \left(n_{2} + 1 \right) - 0.00307 \left(n_{3} + \frac{1}{2} \right) \right] + 1.7 hc(\mathcal{L}^{2} - 1)$$
 (2)

and

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$$W'_{V} = hc \left[1351.2 \left(n_{1} + \frac{1}{2} \right) + 672.2 \left(n_{2} + 1 \right) + 2396.4 \left(n_{3} + \frac{1}{2} \right) \right]$$

$$- 0.3 \left(n_{1} + \frac{1}{2} \right)^{2} - 1.3 \left(n_{2} + 1 \right)^{2} - 12.5 \left(n_{3} + \frac{1}{2} \right)^{2}$$

$$+ 5.7 \left(n_{1} + \frac{1}{2} \right) \left(n_{2} + 1 \right) - 21.9 \left(n_{1} + \frac{1}{2} \right) \left(n_{3} + \frac{1}{2} \right)$$

$$- 11.0 \left(n_{2} + 1 \right) \left(n_{3} + \frac{1}{2} \right) \right]. \tag{3}$$

⁹ D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).

Slight corrections to the listed numerical values have been noted by W. S. Benedict and his collaborators. For the present purposes these corrections are negligibly small. Recent work on frequencies of lines belonging to CO₂ is described in the following papers:
W. S. Benedict, R. C. Herman, and S. Silverman, J. Chem. Phys. 19, 1325 (1951); J. H. Taylor, W. S. Benedict, and J. Strong, Progress Report on "Infrared Spectra of H₂O and CO₂ at 500°C", Contract Nonr. 248-01, The Johns Hopkins University, March 1952.

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Here n_1 , n_2 , and n_3 are the vibrational quantum numbers associated with the fundamental vibration frequencies \mathcal{V}_1 , \mathcal{V}_2 , and \mathcal{V}_3 , respectively. The quantum number \mathcal{L} measures the angular rotation, in units of $h/2\pi$, which is associated with the degenerate (bending) \mathcal{V}_2 -vibration. The rotational energy levels are identified by the rotational quantum number j.

The selection rules for the transitions $n_1 n_2 + n_3 \rightarrow n_1 n_2 + n_3$ may be summarized as follows. For the perpendicular bands, Δn_2 odd, Δn_3 even, $\Delta \mathcal{L} = \pm 1$. For the parallel bands, Δn_2 even, Δn_3 odd, $\Delta \mathcal{L} = 0$. The rotational selection rules are $\Delta j = \pm 1$, 0.

The amplitude facture 8 for given rotational transitions are 11

$$\begin{pmatrix} A_j^j \mathcal{L} \end{pmatrix}^2 = \frac{\mathcal{L}^2}{J(J+1)}$$
(4)

$$\left(A_{j-1}^{j} \ell\right)^{2} = \frac{j^{2} - \ell^{2}}{j(2j+1)} = \frac{2j-1}{2j+1} \left(A_{j}^{j-1} \ell\right)^{2} \tag{4a}$$

$$\left(A_{j}^{j} \mathcal{L}_{+}^{\mathcal{L}}\right)^{2} = \frac{(j \pm \ell)(j \mp \ell + 1)}{4j(j + 1)}, \ell \neq 0, \tag{4b}$$

$$\left(A_{j}^{j} \quad {0 \atop 1}\right)^{2} = 1/2,$$
 (4c)

$$\left(A_{j-1}^{j}, \chi_{+1}^{\ell}\right)^{2} = \frac{(j \pm \ell)(j \pm \ell - 1)}{4j(2j+1)}, \ell \neq 0, \tag{4d}$$

$$\left(A_{j-1}^{j} \ _{1}^{0}\right)^{2} = \frac{j-1}{2(2j+1)} \ , \tag{4e}$$

$$\left(A_{j}^{j-1} \stackrel{\ell}{\ell} \right)^{2} = \frac{(j \pm \ell) (j \pm \ell + 1)}{4j (2j-1)} , \ell \neq 0,$$
 (4f)

The amplitude factors given in Eqs. (4) to (4g) are 4 times as large as those listed by Dennison⁸ because we are using a Fourier series in time of the form cos(2mvt) rather than exp (2mivt).

(49)

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$$\left(A_{j}^{j-1} \ {}^{0}_{1}\right)^{2} = \frac{j+1}{2(2j-1)}$$
 (4g)

In Eqs. (4) to (4g) the convention has been adopted that the amplitude factor corresponding to the transition $j, \ell \longrightarrow j', \ell'$ has been written as $\begin{pmatrix} A_j^{j'} & \ell' \end{pmatrix}$...

The integrated absorption for a given transition from the lower energy level $n_1 n_2 = n_3$; j to the upper energy level $n_1 n_2 = n_3$; j is designated as $S = S(n_1 n_2 = n_3)$; j $\rightarrow n_1 n_2 = n_3$; j and is given by the approximate relation

$$S = (8\pi^{3})N_{T}/3hcQ'_{V}Q'_{R})\left\{ \exp - \left[W'_{V}(n_{1}, n_{2}, n_{3}) + W'_{R}(j, \mathcal{L})\right]/kT\right\}$$

$$\times g_{j'\mathcal{L}'}\left(A_{j}^{j'}\mathcal{L}'\right)^{2} \beta^{2}\left[1 - \exp\left(-h\sqrt{kT}\right)\right]. \tag{5}$$

In Eq. (5) $\mathcal{N} = \mathcal{N}(n_1 \ n_2 \ n_3; j \longrightarrow n_1 \ n_2 \ n_3; j')$ is the Bohr frequency corresponding to the indicated change in the quantum numbers;* $N_T = \text{total}$ number of molecules per unit volume per unit pressure; $g_{j',\ell} = \text{statistical}$ weight of the upper state with $g_{j',\ell'} = 2j' + 1$ for $\ell' = 0$ and $g_{j',\ell'} = 2(2j' + 1)$ for $\ell' \neq 0$; $\beta \neq \beta$ ($n_1 \ n_2 \ n_3 \longrightarrow n_1 \ n_2 \ n_3$) is a factor which must be determined empirically and corresponds to the matrix element of the electric moment in the molecule associated with the indicated change in (vibrational) quantum numbers;* $Q_R = \sum_j \sum_{k} g_{j,k} \exp\left[-W_R(j,\ell)/kT\right] = \text{complete rotational partition function;}$ $Q_V = \sum_{n_1} \sum_{n_2} \sum_{n_3} \exp\left[-W_V(n_1, n_2, n_3)/kT\right] = \text{complete vibrational}$ partition function.

^{*} Although we shall not indicate explicitely the changes in the (vibrational) quantum numbers involved, both ∇ and β do, of course, vary from one vibration-rotation band to another.

The amplitude factors given in Eqs. (4) to (4g) are based on the assumption that vibration-rotation interactions have a negligibly small influence on amplitude factors. For this reason, the use of Eq. (5) involves somewhat cruder calculations than were employed in the calculations on diatomic molecules with non-overlapping rotational lines. ²

For the purposes of approximate radiant heat transfer calculations it is convenient to use the integrated absorption coefficient for a given band. Let

$$\alpha(n_1 n_2 n_3 - n'_1 n'_2 n'_3) = \sum_{j} \sum_{j'} S(n_1 n_2 n_3; j \rightarrow n'_1 n'_2 n'_3; j').$$
 (6)

For the parallel bands $\Delta A = 0$ and $\sum_{j'} g_{j',\ell'} (A_j^{j',\ell})^2 = g_{j,\ell}$ according to the Burger and Dorgelo summation rules, which may be verified by use of Eqs. (4) to (4g) by utilizing the selection rules. Hence we obtain from Eqs. (5) and (6) the useful result

where we have set $W_{V}^{1}(n_{1}n_{2}, n_{3}) + W_{R}^{1}(j, \mathcal{L}) = W_{V}(n_{1}, n_{2}, n_{3}, \mathcal{L}) + W_{R}(j)$,

$$Q_V = \sum_{n_1, n_2, n_3, \ell} \exp(-W_V/kT), Q_V'Q_R' = Q_VQ_R \text{ with } Q_R = \sum_j g_j \exp\left[-W(j)/kT\right],$$

and $g_{j,\ell} = g_{j} \times g_{j,\ell}$. If the assumption is not made that

 $\forall x \forall x \forall (n_1 n_2 + n_3; 0 \rightarrow n_1 n_2 + n_3; 0)$ a slight correction is obtained to Eq. (7). 12, 13

For the perpendicular bands $\Delta \mathcal{L} \neq 0$ and $\sum_{j',l'} (A_j^{j',l'})^2 = g_j \mathcal{L}$.

$$\sum_{j'} g_{j'} \chi_{i}^{-1} (A_{j}^{j'} A_{j}^{\pm 1})^{2} = \frac{1}{2} g_{j} \chi_{i}^{-1} \sum_{j' \in \mathcal{L}_{i}} g_{j' \in \mathcal{L}_{i}}^{-1} (A_{j}^{j'} A_{j}^{i'})^{2} = g_{j} \chi_{i}^{-1}$$
 Hence

$$\times \left\{ \exp - \left[W_{V}(n_1, n_2, n_3, l) / kT \right] \right\} \left[1 - \exp(-h V/kT) \right]$$

where
$$g_{\ell} = 1$$
 for $\ell = 0$ and $g_{\ell} = 2$ for $\ell \neq 0$, (8)

and

$$\langle (\mathbf{n}_1 \mathbf{n}_2 \mathcal{L} \mathbf{n}_3 \rightarrow \mathbf{n}'_1 \mathbf{n}'_2 \mathcal{L}^{-1} \mathbf{n}'_3) = (4\pi^3 \beta^2 \, \mathcal{V}' \, \mathbf{N}_T / 3 \text{heQ}_{\mathcal{V}}) \, \mathbf{g}_{\mathcal{L}}$$

$$\mathbf{z} \left\{ \exp \left[\left[\mathbf{W}_{\mathcal{V}}(\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3, \mathcal{L}) / \mathbf{k} \mathbf{T} \right] \right] \left[1 - \exp(-\mathbf{h} \mathcal{V} / \mathbf{k} \mathbf{T}) \right]$$

$$\text{where } \mathbf{g}_{\mathcal{L}} = 1 \text{ for } \mathcal{L} = 0 \text{ and } \mathbf{g}_{\mathcal{L}} = 2 \text{ for } \mathcal{L} \neq 0. \quad (9)$$

In using Eqs. (8) and (9) it should be noted particularly that the quantities β^2 are generally different for the transitions involving \mathcal{L} — \mathcal{L} + 1 and

B. L. Crawford, Jr., and H. L. Dinsmore, J. Chem. Phys. 18, 983, 1682 (1950).

Eggers and Crawford have shown how to relate for CO, the matrix coefficients to the coefficients of Taylor series expansions of the potential energy and dipole moment about their respective equilibrium values.

 $\mathcal{L} \rightarrow \mathcal{L} - 1$. The ratios of the β^2 can be calculated theoretically to the harmonic oscillator approximation for harmonic bands (see Appendix I for details).

In the same manner as for emissivity calculations on distomic molecules with overlapping rotational lines, 1 we shall find Eq. (5) useful for the determination of "effective band-widths" whereas Eqs. (7) to (9) lead directly to "average absorption coefficients" for vibration-rotation bands. For the calculation of S it may be convenient to combine Eqs. (4) to (4g), (5), and (7) to (9). For example, for the positive branch of the $\sqrt[3]{2}$ - fundamental of CO_2 , we obtain

$$s \simeq \left[\omega(01^{1}0; j \to 00^{0}0; j-1)/\omega(01^{1}0; 0 \to 00^{0}0; 0)\right] \times (\Omega_{R})^{-1}$$

$$\times \alpha(01^{1}0 \to 00^{2}0) \times (j+1) \left[\exp - (W_{R}/kT)\right]$$
 (5a)

where (a) denotes a wave number.

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III. APPROXIMATE EMISSIVITY CALCULATIONS AT 300°K

The positions and approximate intensities of the stronger vibration-rotation bands of CO₂ at 300°K are well-known. ^{5-10, 14} A first approximation to the effective band-width is obtained by utilizing relations such as Eq. (5a) and defining the effective band-width as the wave number range for which S exceeds 10⁻³ of its maximum value. ¹ Utilizing this definition of band-width, which we shall refine presently, a summary of vibration-rotation bands for CO₂ at 300°K has been drawn in Figs. 1 to 3.

G. Hersberg, Infrared and Raman Spectra of Polyatomic Molecules,
D. Van Nostrand Co., New York 1951, Table 56 on p. 274, Herzberg's
designations of band intensities as vs (very strong), s (strong)
m (medium), w (weak), and vw (very weak) has been used in Figs. 1 to 3
to identify the approximate strengths of bands at room temperature.

In these diagrams the abscissa is the wave number whereas the ordinate represents, in arbitrary units which vary from one band to another, the intensity. Integrated intensities at 300 K are given in Table I in so far

Table I. Integrated intensities for vibration - rotation bands of CO₂. ⁷

Band Center (cm-1)	Transition	$\alpha(\text{cm}^{-2}-\text{atmos}^{-1})$
5109	00°0 20°1	0. 426
4984	00°0 12°1	1.01
4861	00°0 04°1	0.272
3716	00°0 10°1	42.3
3609	00°0 02°1	28.5
2349	00°0 00°1	2706
2137 2094 2077	$ \begin{array}{ccc} 01^{1}0 \longrightarrow 20^{\circ}0 \\ 01^{1}0 \longrightarrow 12^{2}0 \\ 00^{\circ}0 \longrightarrow 11^{1}0 \end{array} $. 147
1933 } 1886 }	$ \begin{array}{c} 00^{\circ}0 \longrightarrow 03^{1}0 \\ 01^{1}0 \longrightarrow 04^{\circ}0 \end{array} $. 083
721 668 667 648 618	$ \begin{array}{ccc} 01^{1}0 & \longrightarrow & 10^{\circ}0 \\ 01^{1}0 & \longrightarrow & 02^{2}0 \\ 00^{\circ}0 & \longrightarrow & 01^{1}0 \\ 02^{\circ}0 & \longrightarrow & 03^{1}0 \\ 01^{1}0 & \longrightarrow & 02^{\circ}0 \end{array} $	171.5
961	10°0 00°1	0.0219*
1064	02°0 00°1	0.0532+

^{*} Unpublished data obtained by D. Webur.

as they are available. ⁷ For the strongest bands (\mathcal{D}_2 - and \mathcal{D}_3 - fundamentals) the contributions from the isotopic molecule C^{13} O_2^{16} are also shown. This chemical species constitutes about 1.1 $^{\circ}$ /o of all of the CO_2 present and makes contributions to the total emissivity which are not negligibly small for moderate and large optical densities of emitter. Also shown in Figs. 1 to 3 are the spectral intensities of radiation emitted by a blackbody at 300, 600 and 1500 $^{\circ}$ K, again utilizing arbitrary scales along the ordinates, which are, however, consistent for any one of the given temperatures.

Reference to Fig. 1 shows that the principal contribution to the total radiant heat transfer at room temperature must occur from the spectral region around the \mathcal{V}_2 - fundamental. Thus it is readily shown that the "limiting emissivity" for CO_2 at $300^{\mathrm{O}}\mathrm{K}$ is in the neighborhood of 0.4 with more than 90 $^{\mathrm{O}}/\mathrm{o}$ of the total contributions made by the wave number region extending from 551 to 830 cm $^{-1}$.

It is physically obvious that the engineering emissivity E at 300° K is determined by the $01^{1}0 \longrightarrow 00^{\circ}0$ transition in the limit of zero optical density of the emitter. As was pointed out in an earlier publication, the emissivity as a function of optical density (partial pressure p of emitter x optical pathlength L) for very small values of p L can be computed quite accurately either by utilizing a treatment applicable for non-overlapping lines or by using average absorption coefficients. The emissivity E_{667} of the band with center at 667 cm⁻¹, as calculated from Eq. (30) of Ref. 2a, is plotted as a function of p L in Fig. 4 and labelled "approximation for non-overlapping lines". The corresponding

quantity obtained by using the average absorption coefficient? $PX = (171 \text{ cm}^{-2} \text{ atmos}^{-1})/(106 \text{ cm}^{-1})$ over the effective band-width extending from 600 to 706 cm⁻¹ gives results which are practically identical with those obtained for non-overlapping rotational lines as p L is reduced below about 0.02 ft-atmos. As p L is increased Eq. (30) of Ref. (2a) rapidly fails to apply and yields excessively large values not only for E_{667} but also for the total engineering emissivity E. Needless to say, for p L < 0.02 ft-atmos, the numerical value of E_{667} is to be identified with the value of E.

As the optical density is increased to moderate values of p L, it becomes necessary first to include the $01^{10} \longrightarrow 00^{0}0$ transition for $C^{13} O_{2}^{-16}$, which is assumed to represent i. 1°/o of the total CO_{2} , and for which the integrated intensity is roughly the same as for the $C^{12} O_{2}^{-16}$ species. In treatments using average absorption coefficients it is, of course, necessary to add absorption coefficients rather than emissivities in regions in which partial overlapping between effective band-widths occurs. Finally, the contributions made by the $10^{0}0 \longrightarrow 01^{1}0$ and $02^{0}0 \longrightarrow 01^{1}0$ bands must be included; both of these are designated by Hersberg 14 as being of "medium" intensity whereas the $03^{1}0 \longrightarrow 02^{0}0$ and $11^{1}0 \longrightarrow 02^{2}0$ bands are labelled "weak" and the $11^{1}0 \longrightarrow 02^{0}0$ band is said to be "very weak".

Strictly speaking, room temperature emissivity calculations for CO₂ cannot be carried further because the integrated intensities for the weaker bands are not available. However, it is easily shown that results in fairly good agreement with Hottel's data ⁴ are obtained if reason-

able estimates are made for the strongest of the bands which has not yet been included in determining \mathcal{R} .

It is known from rough unpublished measurements that the integrated intensity α_{721} for the 10°0 --- 0i¹0 band is of the order of 1 cm⁻² atmos⁻¹. Emissivity calculations treating \propto_{721} as a variable parameter between 0 and 10 cm⁻²-atmos⁻¹ are shown in Fig. 4. The curves labelled $\alpha_{721} = 0$, $\alpha_{721} = 1$, and $\alpha_{721} = 10$ with \$\alpha_{667} = 171 correspond to the calculated values of E for the various assumed values of p L. In making these calculations the concept of the effective band-width was refined in so far as the effective band-width for the V_2 - fundamental was set equal to the wave number range for which SpL/0.7 ≥ 0.1. This definition of band-width for strong bands has the important advantage of making the band-width a weak function of pL, in agreement with empirical measurements. 1b The contributions to E made by the $00^{\circ}1 \longrightarrow 10^{\circ}0$ and $00^{\circ}1 \longrightarrow 02^{\circ}0$ bands are very small but have also been included. To these bands Weber assigns the following values at 300° K: $\alpha_{961} = 0.0219 \text{ cm}^{-2} \text{ atmos}^{-1}$, $\propto 1064 = 0.0532 \, \text{cm}^{-2} \, \text{atmos}^{-1}$.

In addition to the calculated emissivities, the results of empirical measurements are also shown in Fig. 4. For p L \leq 0.06 ft-atmos. the "empirical" data are really extrapolated results. Reference to Fig. 4 shows fair agreement between calculated and observed values of E for the reasonable values $\approx 667 = 171$ and $\approx 721 = 1$ cm atmos 1. At very small values of p L the calculated emissivities are larger than

^{*} The dotted curve in Fig. 2 corresponds to $\propto _{667} = 29$ and $\propto _{721} = 1$ cm⁻²atmos⁻¹. Although this curve represents a good fit of the empirical data, the result cannot be considered to be significant since $\propto _{667}$ is known to be much larger than 29 cm⁻²atmos⁻¹.

the extrapolated empirical data but must be considered to be more reliable since they depend only on the numerical value of \bowtie_{667} , which is known with fair accuracy. S-7 Our ability to calculate E at very large values of p L is limited by the lack of adequate intensity data for the transitions $02^00 \longrightarrow 01^10$, $11^10 \longrightarrow 02^20$, and $11^10 \longrightarrow 02^00$. However, it is clear that as p L is increased sufficiently above 3 ft-atmos, E must approach about 0.4 and will then increase only very slowly as exceedingly large values of p L are obtained.

The discussion of emissivity calculations on CO₂ at 300°K as a function of p L is mostly of academic interest. However, it is instructive in so far as it exemplifies the inherent simplicity of the analysis if adequate spectroscopic data are available.

IV. APPROXIMATE EMISSIVITY CALCULATIONS AT 600°K

It is evident from Fig. 2 that the major contributions to radiant heat transfer at 600°K are made by vibration-rotation bands in the spectral region between 890 and 2400 cm⁻¹. As p L goes to zero it is expected that the total emissivity E will become substantially equal to the emissivity of the intense $\sqrt{3}$ - fundamental of $C^{12}O_2^{16}$ with appropriate corrections for contributions from the isotopic species $C^{13}O_2^{16}$. Although we are unable to complete the emissivity calculations at 600° K because the needed spectroscopic data are not available, the engineering emissivity is estimated correctly for small values of p L. This result emphasises the fact that relatively accurate emissivity calculations for polyatemic molecules can be performed without difficulty as soon as the necessary infrared intensity measurements are available.

For the weaker bands, i.e.; for all bands but the V_3 - fundamental, we shall define the effective band-width as the wave number region for which S exceeds about 10^{-3} of its maximum value. For the V_3 - fundamental we set the effective band-width equal to the wave number range for which $(\mathrm{SpL}/0.7) \geqslant 0.1.*$ The long wave-number limit of the V_3 - fundamental is set equal to 2410 cm⁻¹, i.e., 11 cm⁻¹ beyond the band head. This choice allows for the many tails of rotational lines which "spill" across the band-head limit. We proceed by calculating separately the partial emissivities for selected wave number regions.

(A). Contributions of the $00^{\circ}1 \rightarrow 10^{\circ}0$ and $00^{\circ}1 \rightarrow 02^{\circ}0$ Bands

The criterion $(5/5_{\rm max}) > 10^{-3}$ for the weaker bands leads to bandwidths of the order of 140 cm⁻¹ at 600° K. The integrated intensity for a given vibration-rotation band at the arbitrary temperature T, divided by the measured value at 300° K, is obtained by the use of Eqs. (7), (8) or (9). From these relations we find for the integrated intensity \ll of the band whose ground state is identified by the set of quantum numbers $\frac{1}{100^{\circ}}$ the result

^{*} Although the definitions of the effective band-widths are somewhat arbitrary, it is easily shown that calculated values of E are quite insensitive to the chosen band-widths. This result is caused by automatic choice of too small absorption coefficients for band-widths which are too large, and conversely (Compare Ref. la). Use of the quantity SpL/0.7 > 0.1 assures inclusion within the band-width of the V₃-fundamental of all of the rotational lines with average emissivities in excess of 0.1. Substantially the same numerical values for the effective band-widths of the V₃-fundamental are obtained if the lines with SpL/0.7 > 10⁻¹n are included, where n is a number which does not differ from unity by more than a factor of three or four.

where

$$Q_V(T) \exp \left[W_V(00^{\circ}0)/kT \right] \simeq \left[1 - \exp \left(-1388 \text{ hc/kT} \right) \right]^{-1}$$

$$\times \left[1 - \exp \left(-667 \text{ hc/kT} \right) \right]^{-2}$$

$$\times \left[1 - \exp \left(-2349 \text{hc/kT} \right) \right]^{-1}.$$
(11)

The use of Eqs. (10) and (11) leads to the following results for the $80^{\circ}1 \longrightarrow 10^{\circ}0$ and $00^{\circ}1 \longrightarrow 02^{\circ}0$ bands, respectively: $\ll_{961}(600^{\circ}\text{K}) \simeq$ 9. 29 $\ll_{961}(300^{\circ}\text{K}) = 0.204 \text{ cm}^{-2} \text{ atmos}^{-1}$; $\ll_{1064}(600^{\circ}\text{K}) \simeq 7.22 \ll_{1064}(300^{\circ}\text{K}) = 0.385 \text{ cm}^{-2} \text{ atmos}^{-1}$. Hence the total contribution to the emissivity obtained from the two bands under discussion is

$$E_{961} + E_{1064} = 0.052 \left[1 - \exp \left(1.40 \times 10^{-3} \text{ pL} \right) \right]$$

$$+ 0.017 \left[1 - \exp \left(4.15 \times 10^{-3} \text{ pL} \right) \right]$$

$$+ 0.054 \left[1 - \exp \left(2.75 \times 10^{-3} \text{ pL} \right) \right] \quad (12)$$

where pL is expressed in cm-atmos.

(B). Contributions Made by the Bands Between 1800 and 2210 cm⁻¹

0

It is known from the recent work of Taylor, Benedict, and Strong 15 that an appreciable number of vibration-rotation bands, in addition to the bands shown in Fig. 1 in this region, are observable at 500°C.* Since all of these bands involve transitions to excited energy levels, their integrated intensity would be expected to increase as the temperature is raised. Rough absolute intensity estimates for several bands in the 5 micron region are given in Table II at 300 and 600°K. The relative intensity estimates were obtained by using the greatly oversimplified harmonic oscillator approximation described in Appendix I. Thus the contributions of both mechanical and of electrical anharmonicities to the intensity have been neglected.

As is evident from the experimental data shown in Reference 15, a large number of vibration-rotation bands remain for which even rough intensity data are not available. For this reason no result can be given for the contributions made to the engineering emissivity by the vibration-rotation bands between 1800 and 2100 cm⁻¹.

J. H. Taylor, W. S. Benedict, and J. Strong, Progress Report on "Infrared Spectra of H₂O and CO₂ at 500°C", Contract Nonr 248-01, The Johns Hopkins University, Baltimore, Md., March 1952.

^{*} Data of the type presented in Ref. 15 are valuable aide in performing emissivity calculations. For example, the spectroscopic teasemission records indicate, at least qualitatively, the vibration-rotation bands which must be included, at temperatures up to 773° K.

0

Table II. Absolute intensities at 300 and at 600 K for several vibrationrotation bands in the 5 micron region, based on intensity
calculations using harmonic oscillator approximations (Cf.
Appendix I.). The value 0.147 cm⁻²-atmos⁻¹ for the sum of
the bands centered at 2137, 2094, and 2077 cm⁻¹ served as
standard to fix the absolute intensity scale.

Transition	<pre><pre><pre></pre> <pre><pre><pre></pre> <pre><pre></pre> <pre></pre> <pre></pre></pre></pre></pre></pre></pre>	<pre> <at (cm<sup="" 600°k="">-2-atmos⁻¹) </at></pre>
00°0 11 ¹ 0	0.12	0.040
$01^{1}0 \longrightarrow 12^{2}0$	0.020	0.032
01 ¹ 0 20°0	0.0045	0.0075
01 ¹ 0 12°0	0.00048	0. 00079
$02^20 \longrightarrow 13^30$	0.0012	0.0099
$03^30 \longrightarrow 14^40$	0.000038	0.0020
$02^{2}0 \longrightarrow 21^{1}0$	0.00019	0.0015
10°0 21 ¹ 0	0.00029	0. 0026
11 ¹ 0 30°0	0.0000053	0.00026
-	7	

(C). Contributions from the γ_3 - Fundamental

From the measured integrated intensity for the V_3 -fundamental at 300°K and by use of Eqs. (10) and (11) we find $\alpha_{2349} = 1060 \text{ cm}^{-2} \text{atmos}^{-1}$ at 600° K. Of the total integrated intensity per $(\text{cm}^{-1}) \text{k} (\text{cm}^{-1} - \text{atmos}^{-1})$ of CO_2 we associate 98.9°/o with $C^{12}O_2^{16}$ and 1.1°/o with $C^{13}O_2^{16}$. For the intense V_3 -fundamental the effective band-width corresponds to the wave number range $\Delta \omega_{2349}$ for which (SpL/0.7) > 0.1 with the bandwidth of the isotopic species determined similarly. In general, the

 $C^{12}O_2^{16}$ - band is black before the isotopic band makes appreciable contributions. The emissivities at 600° K, E_{2349} , calculated by the use of average absorption coefficients $\vec{P} = \alpha/\Delta\omega$, are summarized in Table III as a function of pL. Comparison of E_{2349} (total) with the

Table III. Emissivities E₂₃₄₉ for C¹²O₂¹⁶ and C¹³O₂¹⁶ at 600°K as a function of optical density. *

pL, cm-atmos.	pL, ft-atmos.	E ₂₃₄₉ (C ¹² O ₂ 16)	E ₂₃₄₉ (C ¹³ O ₂ ¹⁶)	E ₂₃₄₉ (total)
0. 1	0. 0033	0.018	0.0005	0.019
0.5	0.0164	0.033	0.0016	0.035
1.0	0.033	0.037	0.0025	0.040
5.0	0.164	0.050	0.0079	0.057
15	0.492	0.051	0.011	0.062
50	1.64	0.052	0.01i	0.063
100	3. 28	0.053	0.012	0.065
200	6,56	0.055	0.012	0.067

* The tabulated values of $E_{2349}(C^{13}O_2^{16})$ correspond to the values which must be added to $E_{2349}(C^{12}O_2^{16})$ in order to obtain E_{2349} (total). They do not include emissivities in the (black) region of the \aleph_3 -fundamental of $C^{12}O_2^{16}$ which is overlapped by the \aleph_3 -fundamental of $C^{13}O_2^{16}$.

empirical data 4 plotted in Fig. 5 shows that for pL \leqslant 0.033 ft.-atmos, E_{2349} (total) is practically identical with the engineering emissivity E.

The result is in accord with expectations and shows clearly that useful emissivity data can be obtained with practically no analytical work once the physical principles are understood clearly.

(D). Contribution of the $02^{\circ}1 \longrightarrow 00^{\circ}0$ and $10^{\circ}1 \longrightarrow 00^{\circ}0$ Bands From the measured integrated intensities we find $\alpha_{36.09}$ =

9.70 cm⁻²atmos⁻¹ for the 02⁰1 \rightarrow 00⁰0 - band and \propto_{3716} = 14,4 cm⁻²atmos⁻¹ for the 10⁰1 \rightarrow 00⁰0 - band at 600⁰K. The effective band-widths extend from 3539 cm⁻¹ to 3679 cm⁻¹ and from 3646 cm⁻¹ 3716 cm⁻¹, respectively. Using average absorption coefficients the following results is obtained:

$$E_{3609} + E_{3716} \simeq 0.0047 \left[1 - \exp(-6.92 \times 10^{-2} \text{ pL}) \right]$$

$$+ 0.0017 \left[1 - \exp(-1.72 \times 10^{-1} \text{ pL}) \right]$$

$$+ 0.0017 \left[1 - \exp(-1.03 \times 10^{-1} \text{ pL}) \right]. \quad (13)$$

(E). The Total (Engineering) Emissivity

(

The total (engineering) emissivity is obtained by adding the partial emissivities from selected spectral regions. Since estimates of partial emissivities were not included for all of the important vibration-rotation bands, no general expression for the engineering emissivity can be given although useful results have been obtained for small values of the optical density (compare § EEC and Fig. 5).

APPENDIX I. RELATIVE INTENSITY CALCULATIONS FOR CO₂ USING HARMONIC OSCILLATOR APPROXIMATIONS*

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It is well known that harmonic bands with non-zero matrix components are predicted even to the harmonic oscillator approximation.

Calculations of this sort are useful for rough relative intensity estimates although mechanical as well as electrical anharmonicity corrections are neglected. Representative relative intensity estimates have been given, for example, by Benedict 15 and by Kaplan. 16 For the present applications it will be convenient to present a general equation for relative intensities of harmonic bands involving changes in the vibrational quantum number \bigvee_2 .

The desired result is obtained readily by using the normalised wave functions for the isotropic plane oscillator and an integral involving associated Laguerre polynomials first obtained by Schrödinger. ¹⁷ In this manner it is easily shown that

$$\left[k! \ k! / (k+\ell)^{\frac{2}{3}} (p!)^{2} \left(\sum_{t=0}^{4k,k!} \binom{p-\ell}{k-t} \binom{p-\ell}{k-t} \binom{p-\ell}{t}^{-p-1} \binom{p-\ell}{t}^{2} \right) \right]^{2}$$

$$\left[k! \ k! / (k+\ell)^{\frac{2}{3}} (p!)^{2} \left(\sum_{t=0}^{4k,k!} \binom{p-\ell}{k-t} \binom{p-\ell}{t-t} \binom{p-\ell}{t}^{-p-1} \right)^{2} \right]$$

$$(A-1)$$

The author is indebted to Drs. W. S. Benedict and L. D. Kaplan for helpful correspondence concerning intensity estimates for harmonic bands of CO₂.

¹⁶ L. D. Kaplan, J. Chem. Phys. <u>18</u>, 186 (1950).

¹⁷ E. Schrödinger, Ann. d. Physik. 80, 483 (1926).

where $k = (1/2) (n_2 - \mathcal{S})$, $k' = (1/2) (n_2 - \mathcal{S})$, $p = (1/2) (\mathcal{S} + \mathcal{S}' + 1)$, and $\binom{n}{k}$ denotes a binomial coefficient.

By combining Eqs. (7) to (9) with Eq. (A-1) the following useful result is obtained:

$$\propto (n_{1}n_{2}^{\ell} n_{3} \rightarrow n_{1}n_{2}^{\prime} n_{3}^{\ell}) / \propto (n_{1} \ 0^{\circ}n_{3} \rightarrow n_{1}^{1} n_{3}^{1}) = \ell(n_{2}^{\ell} \rightarrow n_{2}^{\prime})$$

$$= g_{\ell} R(n_{2}^{\ell} \rightarrow n_{2}^{\prime}) \left[\gamma(n_{1}n_{2}^{\ell} n_{3} \rightarrow n_{1}n_{2}^{\prime} n_{3}^{\prime}) / \gamma(n_{1} \ 0^{\circ}n_{3} \rightarrow n_{1}^{1} n_{3}^{\prime}) \right]$$

$$= \left[W_{V} (n_{1}, n_{2}, n_{3}, \ell) - W_{V} (n_{1}, 0, n_{3}, 0) \right] / kT$$

$$= \left[-h \gamma(n_{2}^{\ell} \rightarrow n_{2}^{\prime} n_{3}^{\prime}) / kT \right] \times \left\{ 1 - \exp\left[-h \gamma(0^{\circ} \rightarrow 1^{1}) / kT \right] \right\}^{-1} (A-2)$$

Numerical values of $R(n_2 \rightarrow n_2^{-1})$ calculated from Eq. (A-1) are identical with Benedict's estimates, ¹⁵ which utilized data given by Shaffer. ¹⁸

Following Benedict we shall assume that resonance between $2 V_2$ and V_1 is exact, an approximation which will not change the order of magnitude of the calculated results although it is not in accord with observed infrared and Raman intensities. By utilizing Eqs. (A-1) and (A-2) relative intensities have been computed for a number of bands in the 5μ region at 300 and at 600° K. The results are summarized in Table (A-1).

¹⁸ W. H. Shaffer, Rev. Mod. Phys. 16, 245 (1944).

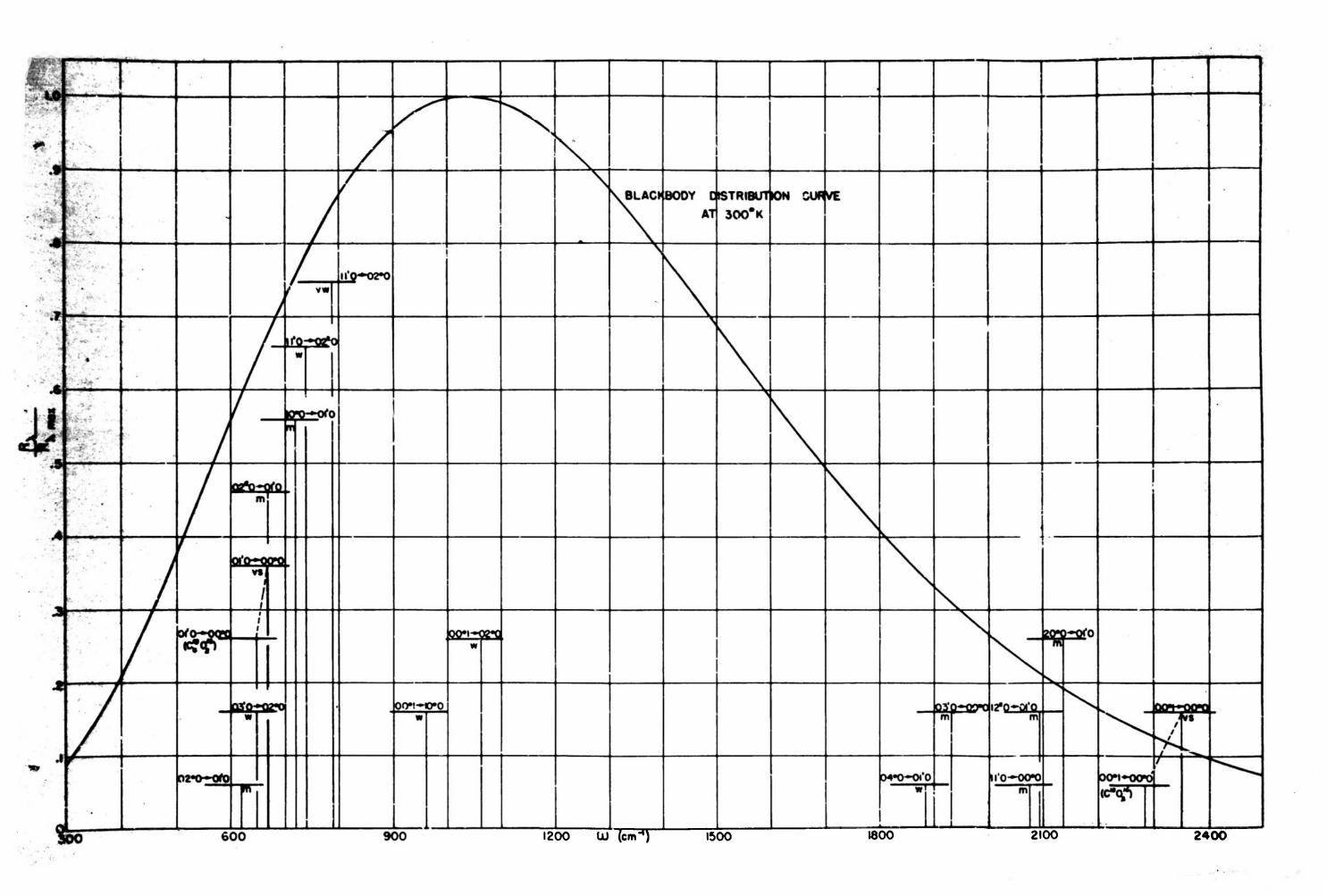
Table (A-1). Relative intensities for harmonic bands in the 5µ region based on harmonic oscillator wave functions.

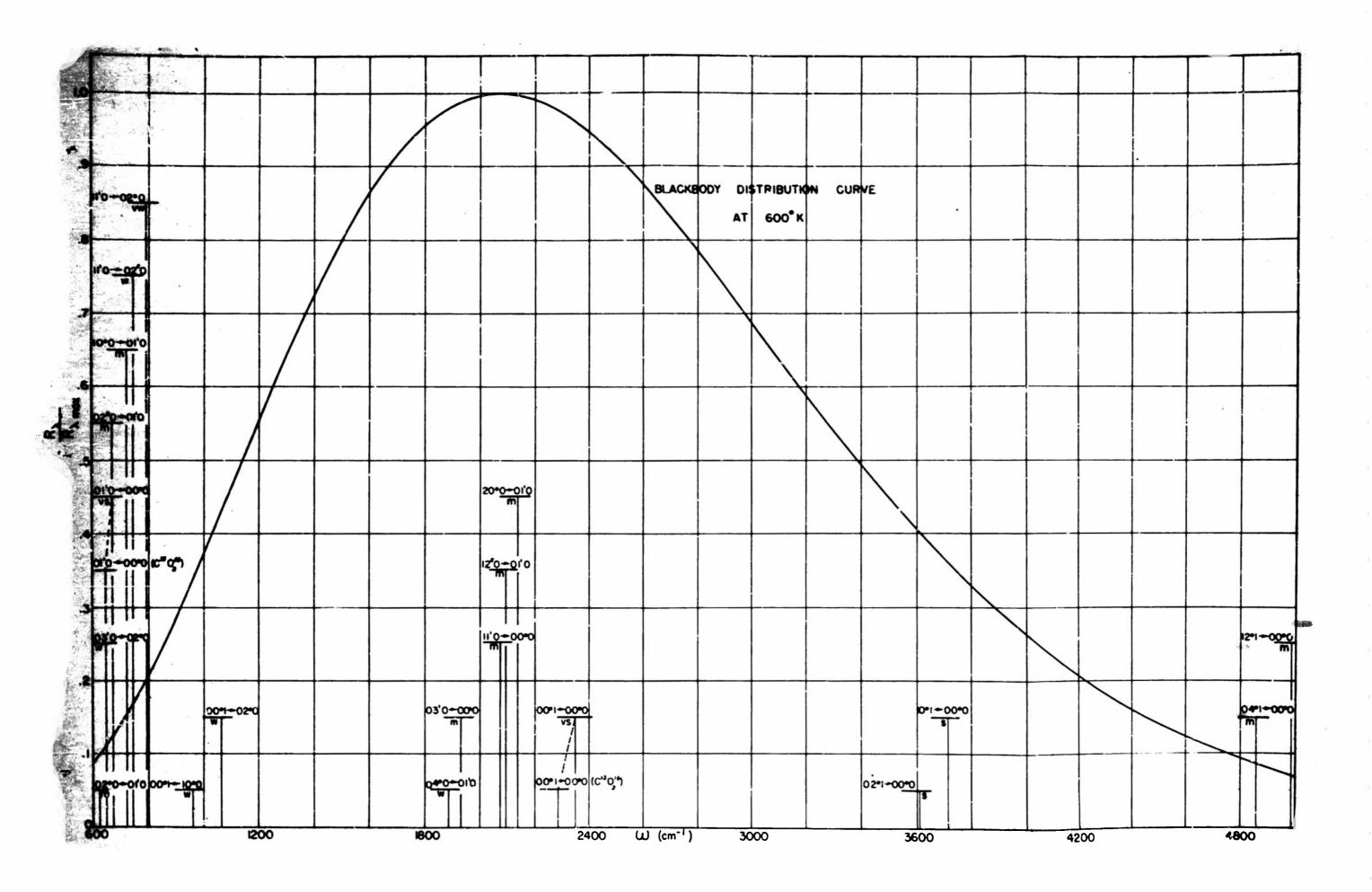
Transition	84R(n ₁ n ₂ ^{4.0} -n' ₁ n' ₂ '0)	0) 8(n1n2 0-n'1n'2'0) at 300°K 6(n1n2 40-n'1n' 2'	6(n ₁ n ₂ L 0 - n' ₁ n' ₂ L' 0) at 600°K
0000-1110	1	1	
$01^{1}0 - 12^{2}0$	•	0.164	0.810
010 - 200	•6.0	0.0376	. 0.187
01 0 - 120	0.1*	0,00395.	0.0196
$02^{2}0 - 13^{3}0$	•	0.0101	0.248
0330-1440	6	0.000315	0.0507
0220 210	*6.0	0.00155	. 0.0382
1000-210	1.0*	0.00238	0.0656
11 0 30 0	*6.0	0.0000438	0.00638

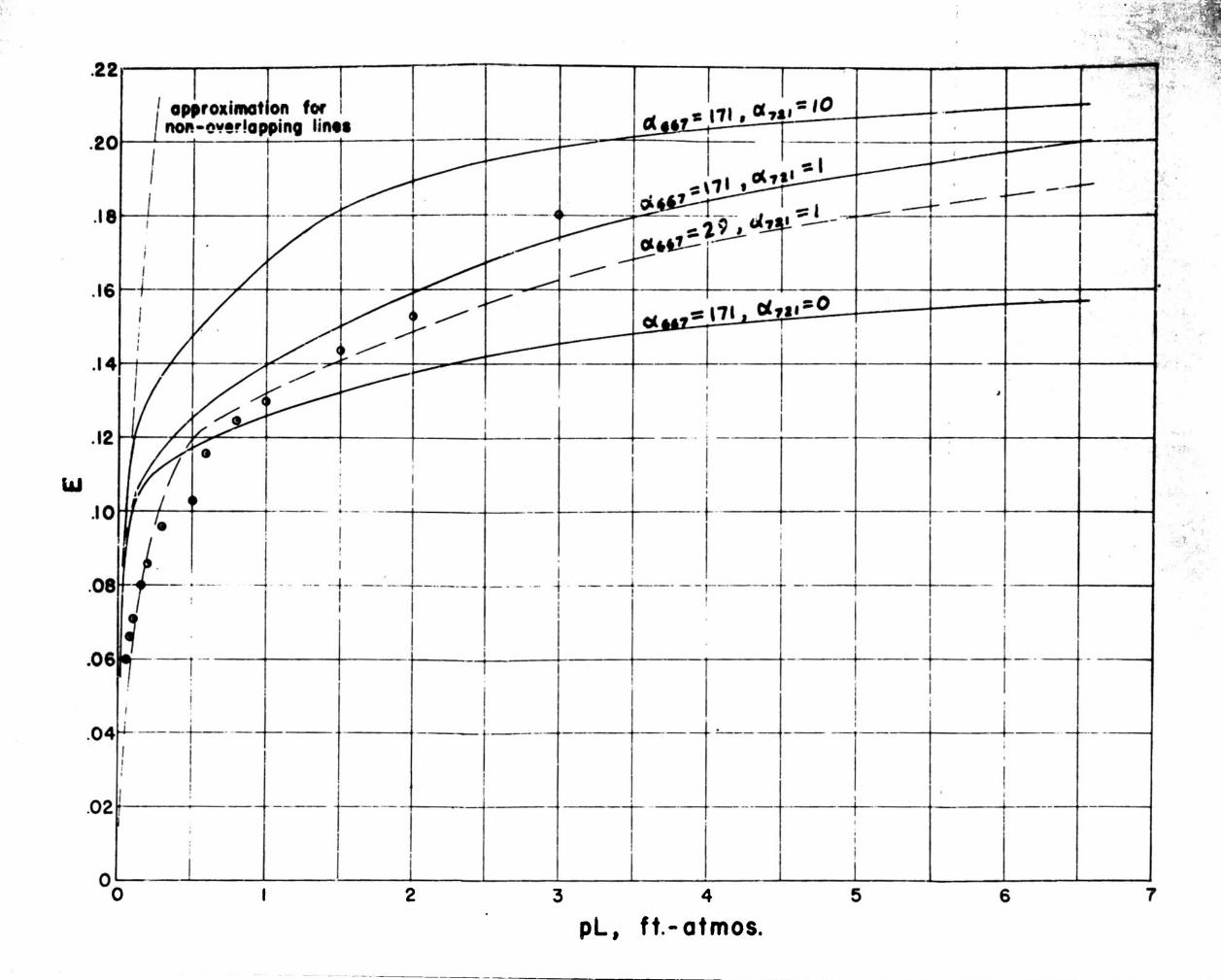
Adjusted according to Benedict to concentrate most of the intensity of resonating bands in the highest frequency member. 15

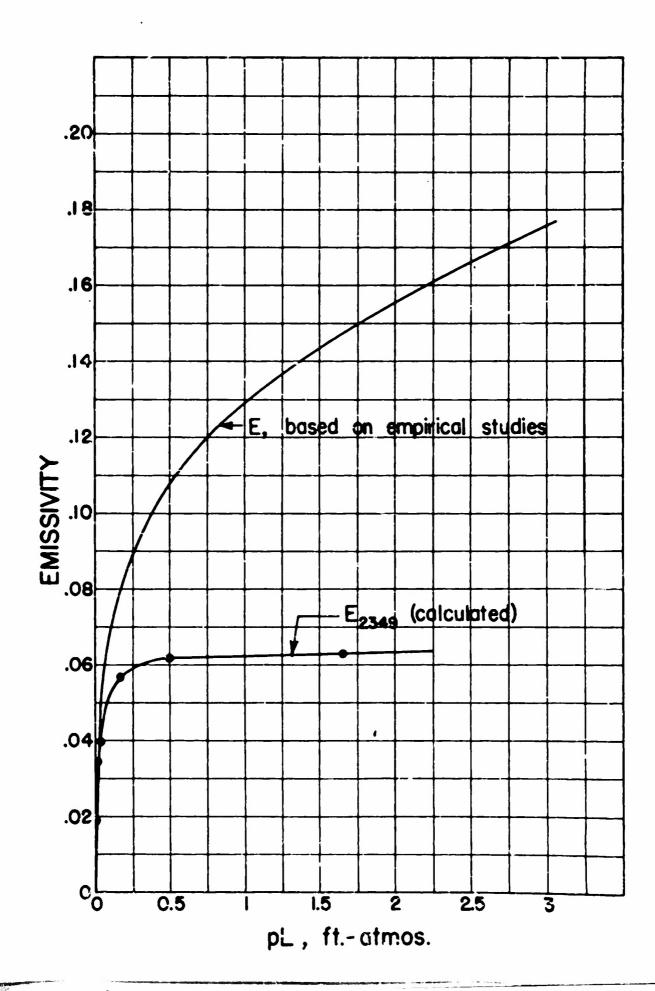
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- Fig. 1. Positions of centers of vibration-rotation bands observed at room temperature between 300 and 2400 cm $^{-1}$. The designations vs (very strong), s (strong), m (medium), w (weak), and vw (very weak) are those of Hersberg. Also shown is the intensity ratio R_{λ}/R_{λ} max for a blackbody at 300°K.
- Fig. 2. Positions of centers of vibration-rotation bands observed at room temperature between 600 and 4800 cm⁻¹. Also shown is the intensity ratio $R \chi / R \chi$ max for a blackbody at $600^{\circ} K$.
- Fig. 3. Positions of centers of vibration-rotation bands observed at room temperature between 1500 and 12,000 cm⁻¹. Also shown is the intensity ratio R_{λ}/R_{λ} max for a blackbody at 1500° K.
- Fig. 4. Engineering emissivity E as a function of pL for CO₂ at 300°K. Integrated intensities of are expressed in cm⁻²-atmos⁻¹. The results based on empirical measurements (Cf. reference 4) are shown as circles.
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